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(54) Luminescent material, especially for LED application

(57) UV-blue excitable green luminescent material consisting of a Eu-doped oxynitride host lattice with general composition $MSi_2O_2N_2$, wherein M is at least one of an alkaline earth metal chosen from the group Ca, Sr, Ba.

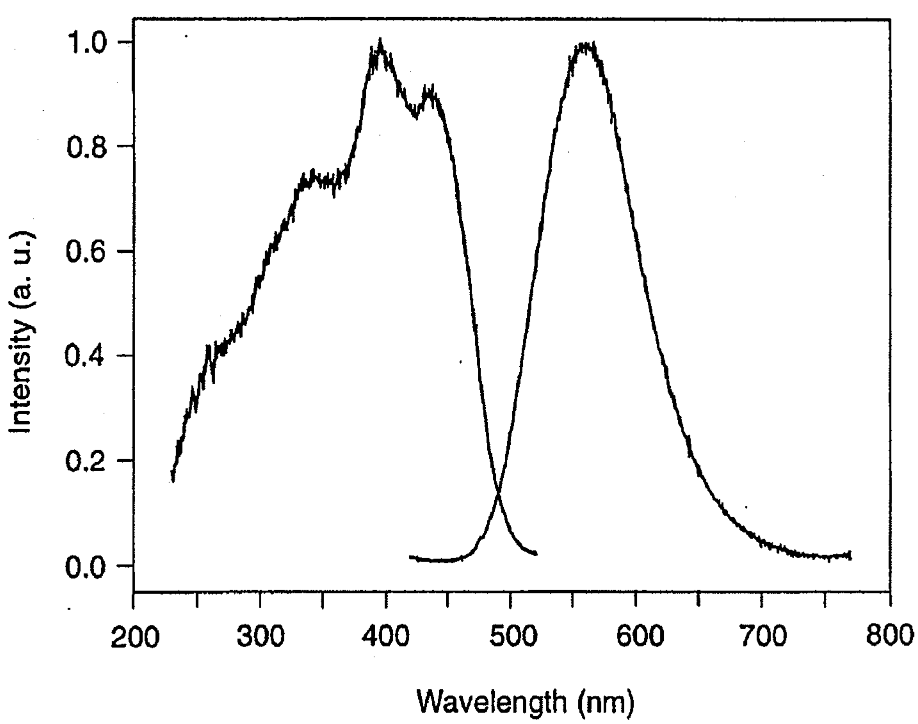

FIG. 3

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Description

Technical Field

[0001] This invention relates to a luminescent material which is excitable in the UV-blue part of the spectral region, and more particularly, but not exclusively to a phosphor for light sources, especially for Light Emitting Diodes (LED). The phosphor belongs to the class of rare-earth activated silicon oxynitrides.

Background Art

[0002] So far white LEDs were realized by combining a blue-emitting diode with a yellow emitting phosphor. Such a combination has a poor color rendition, which, however, can be improved significantly by using a red-green-blue system (RGB). Such a system uses for example a red and blue emitter in combination with a green-emitting aluminate phosphor, like $SrAl_2O_4$:Eu or $BaAl_2O_4$:Eu, with the possible addition of Mn to Eu, whose emission maximum is around 520 nm, see US-A 6 278 135. However, the position of the excitation and emission bands of theses aluminates is not optimum. They have to be excited by short UV in the range of 330 to 400 nm.

[0003] On the other hand, some phosphors derived from the class of MSiON are known; see e.g. "On new rare-earth doped M-Si-Al-O-N materials" by van Krevel, TU Eindhoven 2000, ISBN 90-386-2711-4, Chapter 6. They are doped with Tb. Emission is achieved upon excitation by 365 nm or 254 nm.

Disclosure of the Invention

[0004] It is an object of the present invention to provide a new luminescent material. A further object is to provide a phosphor with a fine-tuned green emission which can be efficiently excited by UV/blue radiation. A further object is to provide a phosphor for use in an illumination device with at least one LED as light source, the LED emitting primary radiation in the range from 380 to 470 nm, this radiation being partially or completely converted into longer-wavelength radiation by such phosphors which are exposed to the primary radiation of the LED. A further object is to provide an illumination device which emits white light and in particular has a high color rendering. A further object is to provide a high-efficiency illumination device like a LED device which absorbs well in the range from 380 to 470 nm and is easy to produce.

[0005] These objects are achieved by the characterizing features of claim 1 and 8, respectively. Particularly advantageous configurations are given in the dependent claims.

[0006] The conversion is achieved at least with the aid of a phosphor which originates from the class of the Eu- or Eu,Mn-coactivated silicone oxynitrides. In more detail, a novel phosphor material is created by doping $MSi_2O_2N_2$ (M = Ca, Sr, Ba) host lattices with Eu ions. The obtained phosphors show high chemical and thermal stability. More extended fine tuning of all relevant properties can be obtained by at least partial replacement of the group (SiN) by (AlO). Preferably, the metal M is Ca or at least mainly Ca with minor additions of Ba and/or Sr for a green-emitting material which can be efficiently excited with blue radiation. The incorporation of nitrogen increases the degree of covalent bonding and ligand-field splitting. As a consequence this leads to a shift of excitation and emission bands to longer wavelengths compared to oxide lattices. The obtained phosphors show high chemical and thermal stability.

[0007] More extended fine tuning of all relevant properties can be obtained by use of a cation M which is achieved by combining several of said M metals, by further addition of Zn as part of cation M, and/or at least partial replacement of Si by Ge. The amount of Eu doped to cation M is between 0,1 and 25 %, preferably between 2 and 15%. In addition further doping with Mn for fine-tuning of relevant properties is possible with an preferred amount of at most 50% of the Eu doping.

[0008] Since these materials can convert UV-blue radiation into green light due to low-energy excitation bands, they can be applied for example in white light sources (e.g. lamps), especially based on primarily blue-emitting LEDs (typically based on GaN or InGaN with emission around 430 to 470 nm) combined with a red-emitting phosphor. A suitable red-emitting phosphor is a Eu-doped silicon nitride material, like $M_2Si_5N_8$ (M = Ca, Sr, Ba), see for example WO 01/40403. Also application for colored light sources is possible.

Brief Description of the Drawings

[0009] In the text which follows, the invention is explained in more detail with reference to a plurality of exemplary embodiments. In the drawings:

Figure 1 shows a semiconductor component (LED) which serves as light source for white light, with casting resin (Figure 1a) and without casting resin (Figure 1b);

Figure 2 shows an illumination device with phosphors in accordance with the present invention;

Figure 3 to 5 show the emission spectra and reflection spectra of phosphors in accordance with the present invention.

Best Mode for Carrying Out the Invention

[0010] By way of example, a structure similar to that used in WO 01/40403 is described for use in a white LED together with an InGaN chip. The structure of such a light source for white light is specifically shown in Figure 1a. The light source is based on a semiconductor component (chip 1) of type InGaN with a peak emission wavelength of 400 nm, having a first and a second electrical connection 2,3, which is embedded in an opaque base housing 8 in the region of a recess 9. One of the connections 3 is connected to the chip 1 via a bond-ing wire 4. The recess has a wall 7 which serves as reflector for the blue primary radiation of the chip 1. The recess 9 is filled with a potting compound 5 which contains a silicone casting resin (or epoxy casting resin) as its main constituents (pref. at least 80 % by weight) and further comprises phosphor pigments 6 (pref. less than 15% by weight). There are also further small amounts of, inter alia, methyl ether and Aerosil. The phosphor pigments are a mixture of three pigments which emit blue, green and red light with the green phosphor being in accordance with the invention.

[0011] Fig. 1b shows an embodiment of a light source with a semiconductor component 10 in which the conversion into white light is effected by means of phosphor conversion layers 16 which are applied directly to the individual chip. On top of a substrate 11 there are a contact layer 12, a mirror 13, a LED chip 14, a filter 15 and a phosphor layer 16, which is excited by the primary radiation of the LED, and converts it into visible long-wave radiation. This structural unit is surrounded by a plastic lens 17. Only the upper contact 18 of the two ohmic contacts is illustrated. Primary UV radiation of the LED is around 400 nm and secondary radiation is emitted by a first phosphor in accordance with the invention using $BaSi_2O_2N_2$:Eu emitting around 500 nm and by a second phosphor using a Nitridosilicate emitting orange-red.

[0012] Figure 2 shows an illumination device 20. It comprises a common support 21, to which a cubical outer housing 22 is adhesively bonded. Its upper side is provided with a common cover 23. The cubical housing has cutouts in which individual semiconductor components 24 are accommodated. They are blue emitting light-emitting diodes with a peak emission of around 450 to 470 nm. The conversion into white light takes place by means of conversion layers 25 which are arranged on all the surfaces which are accessible to the blue radiation. These include the inner surfaces of the side walls of the housing, of the cover and of the support. The conversion layers 25 consist of phosphors which emit in the red spectral region, and in the green spectral region using a phosphor according to the invention and mixing up together with the non-absorbed part of the primary radiation blue primary into white light.

[0013] Eu_2O_3 (with purity 99.99%), $BaCO_3$ (with purity > 99.0%), $SrCO_3$ (with purity > 99.0%), $CaCO_3$ (with purity > 99.0%), SiO_2 and Si_3N_4 were used as commercially available starting materials for the production of the new inventive phosphors. The raw materials were homogeneously wet-mixed in the appropriate amounts by a planetary ball mill for 4-5 hours in isopropanol. After mixing the mixture was dried in a stove and ground in an agate mortar. Subsequently, the powders were fired in molybdenum crucibles at 1100-1400 °C under a reducing nitrogen/hydrogen atmosphere in a horizontal tube furnace. After firing, the materials were characterized by powder X-ray diffraction (copper K-alpha line).

[0014] All samples show efficient luminescence under UV-blue excitation with emission maxima in the blue-green (in case of M = Ba), green (M = Ca) or yellow-green (M = Sr). Typical examples of emission and excitation spectra can be seen in Fig. 3 (M = Ca), Fig. 4 (M = Sr) and Fig. 5 (M = Ba). For $CaSi_2O_2N_2$:Eu a green-emitting phosphor (560 nm peakemission) is obtained, which can be efficiently excited in the blue part of the spectrum (excitation maximum at about 440 nm). By using a mixed compound with M = (Ba,Sr) and varying the proportion of Ba and Sr, the emission can be shifted in the range 500-570 nm, while the top of the excitation band can be shifted from 400 nm up to 430 nm. The observed shift to higher wavelengths is ascribed to a center of gravity of the Eu 5d band at lower energy and a stronger ligand-field splitting of the Eu 5d band. Additional manipulation can be achieved by at least partial replacement (for example up to 15 mol-%) of (SiN) by (AlO), resulting in a preferred structure $MSi_{2-x}O_{2+x}Al_xN_{2-x}$:Eu (e.g. x = 0,15).

[0015] Since these materials can convert UV-blue radiation into green light due to low-energy excitation bands, they can be applied in white light sources, for example based on primarily blue-emitting LEDs (typically GaN or InGaN) combined with a red-emitting phosphor.

[0016] Additional fine tuning can be achieved by incorporation of Zn as an addition to cation M, preferably not more than 30%, and at least partial replacement of Si by Ge, preferably not more than 25 %.

Table 1

Raw materials	Grade
MCO_3 (M = Ca, Sr, Ba)	99.0%
SiO_2	Aerosil OX50
γ-Al_2O_3	> 99.995
Si_3N_4	β content: 23.3%, O~0.7%
Eu_2O_3	99.99%

[0017] In the following the synthesis procedures are given. Possible starting materials are shown in table 1.

[0018] All the oxynitride phosphors can be synthesized according to the following reaction equation:

$$(1\text{-}y)\ MCO_3 + \tfrac{1}{2}\ Si_3N_4 + \tfrac{1}{2}\ SiO_2 + (y/2)\ Eu_2O_3 \rightarrow M_{1\text{-}y}Eu_ySi_2O_2N_2$$

with (M = Ca, Sr, Ba). For example y = 0,1.

[0019] The powder mixture is fired for several hours in Mo crucibles at 1100-1400 °C in a reducing atmosphere of mainly N_2 with small amounts of H_2 (10%) in horizontal tube furnaces.

[0020] With the atomic radius decreasing from Ba to Ca it was found that the replacement of $(SiN)^+$ by $(AlO)^+$ by this reaction became easier.

[0021] Figure 3 shows a typical emission/excitation spectra of $CaSi2O_2N_2$:Eu.

[0022] Figure 4 shows a typical emission/excitation spectra oE $SrSi_2O_2N_2$:Eu.

[0023] Figure 5 shows a typical emission/excitation spectra of $BaSi_2O_2N_2$:Eu.

[0024] Doping with Eu was 10% of cation M in all embodiments.

[0025] The peak emission for M = Ca was around 560 nm, and for M = Sr it was around 570 nm, and for M = Ba it was around 500 nm.

Claims

1. Luminescent material, preferably a phosphor for LED-applications, which is excitable in the UV-blue region from 380 to 470 nm, **characterized by** a Eu-doped host lattice with general composition $MSi_2O_2N_2$, wherein M is at least one of an alkaline earth metal chosen from the group Ca, Sr, Ba and with a proportion of Eu from 0,1 to 30% of M.

2. UV-blue excitable luminescent material according to claim 1, wherein M is Calcium in order to achieve green emission.

3. UV-blue excitable luminescent material according to claim 1, wherein M is a mixture of at least two of these metals.

4. UV-blue excitable luminescent material according to claim 1, wherein M comprises in addition Zn, preferably up to 40 mol-%.

5. UV-blue excitable luminescent material according to claim 1, wherein Si is replaced fully or partially by Ge, preferably up to 25 mol-%.

6. UV-blue excitable luminescent material according to claim 1, wherein the host material is further doped with Mn, the amount of Mn being preferably at most up to 50% of the Eu doping.

7. UV-blue excitable luminescent material according to claim 1, wherein SiN is replaced partially by AlO.

8. Light source (20) with a UV-blue excitable luminescent material according to one of the preceding claims.

9. Light source according to claim 8, wherein the primary emitted light is blue and the UV-blue excitable luminescent material according to claims 1-7 is combined with other phosphors, esp. a red emitting phosphor, in order to convert

part of the primary emitted light into secondary emitted light of longer wavelength resulting in emitting white light.

10. Light source according to claim 8, wherein the primary emitted radiation is UV and the UV-blue excitable luminescent materials according to claims 1-7 are combined with other phosphors, esp. a red and a blue emitting phosphor, in order to convert the primary emitted radiation into secondary emitted light of longer wavelength resulting in emitting white light.

11. Light source according to claim 8, wherein the light source is an illuminating device with at least one LED.

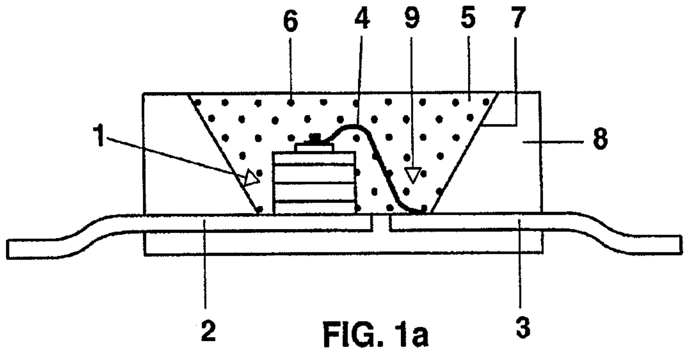


FIG. 1a

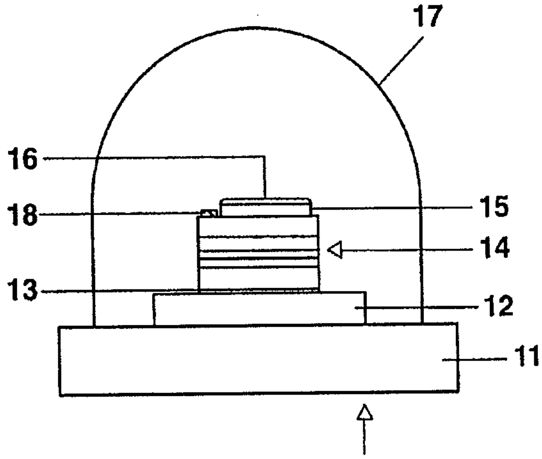


FIG. 1b

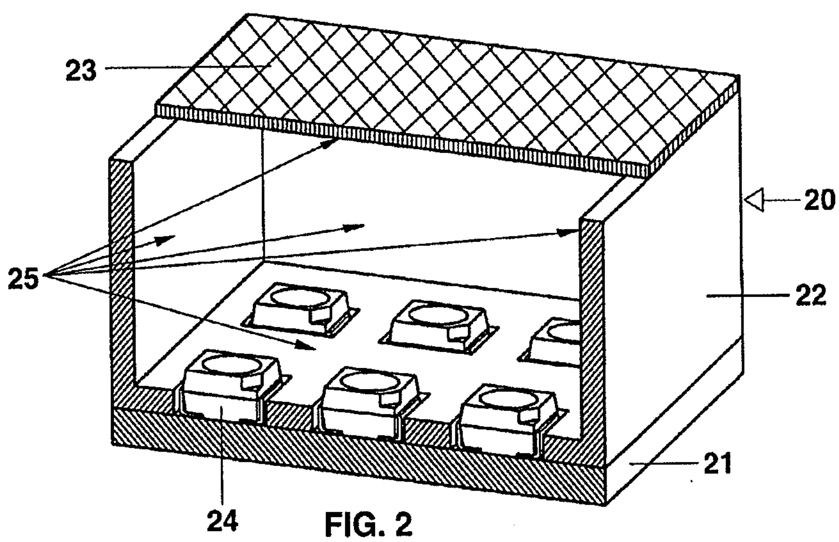


FIG. 2

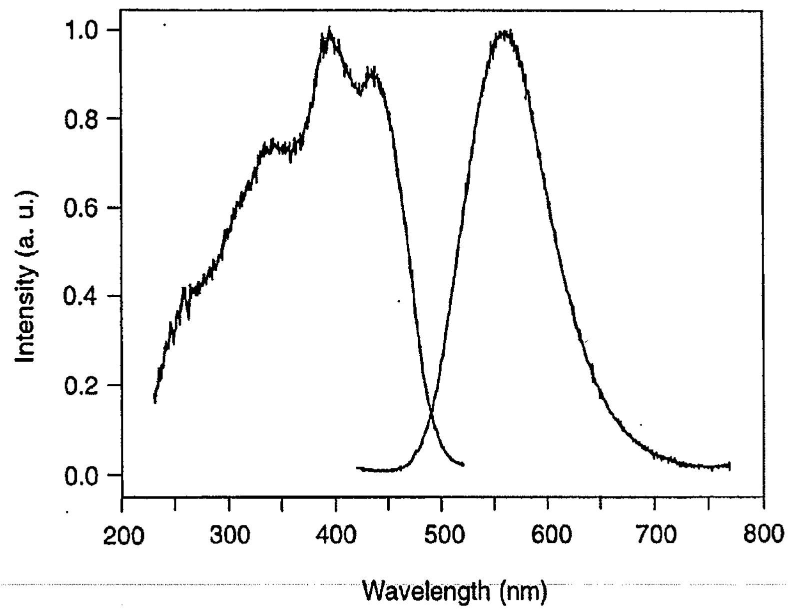
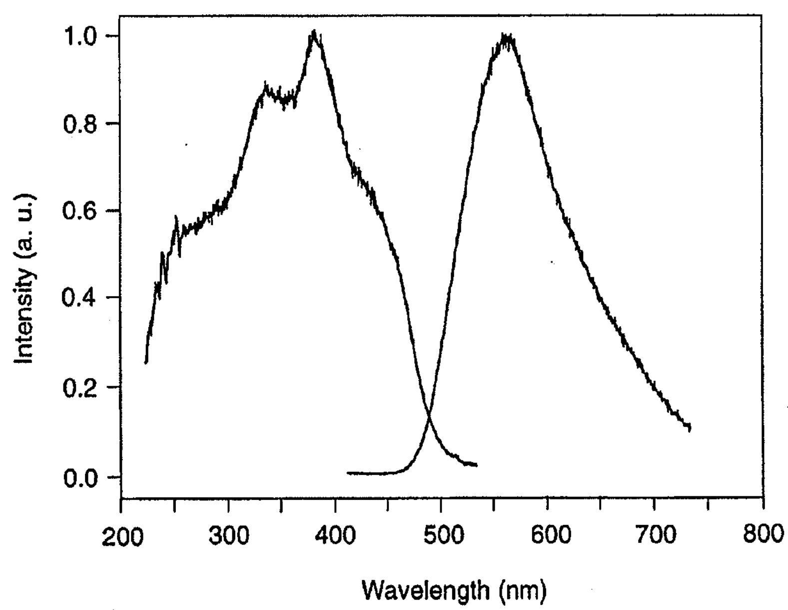

1.0
0.8
0.6
0.4
0.2
0.0
Intensity (a. u.)
200
300
400
500
600
700
800
Wavelength (nm)

FIG. 3


1.0
0.8
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Intensity (a. u.)
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Wavelength (nm)

FIG. 4

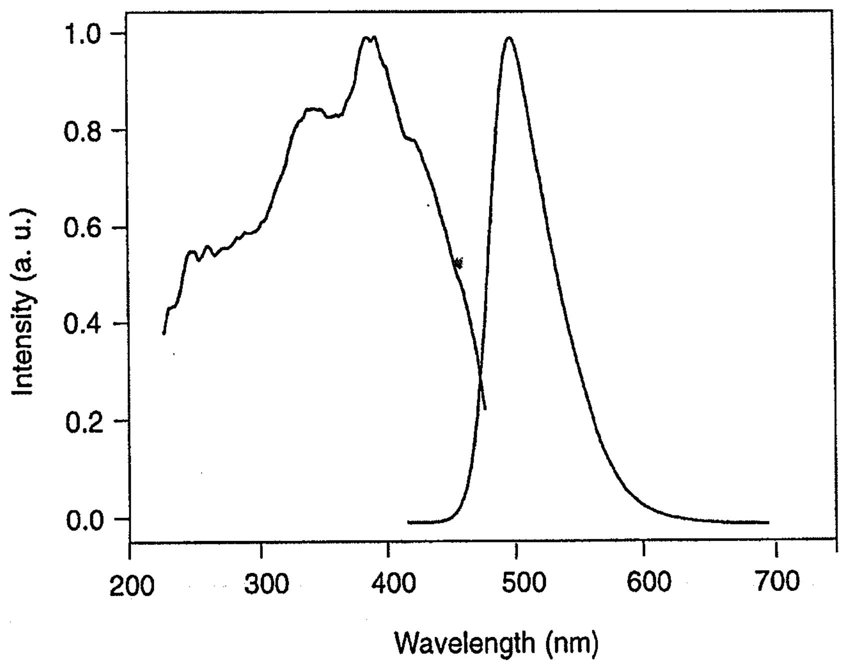
1.0
0.8
0.6
0.4
0.2
0.0
Intensity (a. u.)
200
300
400
500
600
700
Wavelength (nm)

FIG. 5

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EUROPEAN SEARCH REPORT

Application Number
EP 02 02 1172

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	US 6 255 670 B1 (DUGGAL A ET AL) 3 July 2001 (2001-07-03) * the whole document *	1-4,6, 8-11	C09K11/465 C09K11/477 H01L33/00
A	EP 1 193 306 A (SUMITOMO CHEMICAL CO) 3 April 2002 (2002-04-03) * claim 1 *	1,3-6	
A	EP 1 104 799 A (PATRA PATENT TREUHAND) 6 June 2001 (2001-06-06) * claims 1,6 *	1,4,5	
A	US 2002/043926 A1 (KAGA K ET AL) 18 April 2002 (2002-04-18) * the whole document *	1,7-11	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)
C09K
H01L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	5 June 2003	van der Linden, J.E.

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05-06-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6255670 B1	03-07-2001	US 6294800 B1	25-09-2001
EP 1193306 A	03-04-2002	CN 1345908 A	24-04-2002
		EP 1193306 A2	03-04-2002
		JP 2002332481 A	22-11-2002
		US 2002038861 A1	04-04-2002
EP 1104799 A	06-06-2001	EP 1104799 A1	06-06-2001
		CA 2359896 A1	07-06-2001
		CA 2360330 A1	07-06-2001
		CN 1337988 T	27-02-2002
		CN 1337989 T	27-02-2002
		WO 0140403 A1	07-06-2001
		WO 0139574 A1	07-06-2001
		EP 1238041 A1	11-09-2002
		EP 1153101 A1	14-11-2001
		HU 0105080 A2	29-04-2002
		HU 0200436 A2	29-06-2002
		US 2003024438 A1	06-02-2003
		US 2003020101 A1	30-01-2003
US 2002043926 A1	18-04-2002	JP 2002076434 A	15-03-2002

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